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(21) International Application Number: PCT/US98/18169 (22) International Filing Date: 14 September 1998 (14.09.98) (30) Priority Data: 08/948,358 10 October 1997 (10.10.97) US (71) Applicant: CONTRACT MATERIALS PROCESSING, INC. [US/US]; 1922 Benhill Avenue, Baltimore, MD 21226 (US). (72) Inventors: ALBERS, Edwin, W.; 1922 Benhill Avenue, Baltimore, MD 21226 (US). BURKHEAD, Harry, W., Jr.; 1922 Benhill Avenue, Baltimore, MD 21226 (US). (74) Agent: WISE, L., Gene; Suite 101, 1364 Beverly Road, McLean, VA 22101-3628 (US).		(81) Designated States: AU, CA, JP, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: SOLID PARTICLE MANUFACTURE (57) Abstract A method for making solid particles containing a mixture of solid crystalline metal oxide and/or salt compounds comprising the steps of: admixing particulate metal compounds to form a dry solids blend of at least two different crystalline solids; comminuting coarse, dry blended particulate solids, preferably in a micronizer mill by impelling the solids blend with high pressure dry inert gas against a hard plate surface, thereby producing finely-divided crystalline solids; recovering a comminuted solids blend having an average particle size of about 1-5 microns; forming an aqueous slurry of the comminuted solids blend, preferably having a weight ratio of free water to solids less than 2:1; drying the aqueous slurry to form agglomerated particles having an average size range greater than about 20 microns; and recovering dry agglomerated particles having enhanced attrition resistance and particle size uniformity. This manufacturing method is particularly useful in making multi-component contact solids.		

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SOLID PARTICLE MANUFACTURE

FIELD OF THE INVENTION

This invention relates to methods for making mixed crystalline solid particles by dry-milling a mixture of coarse particulate metal oxide and/or metal salt raw materials, forming a slurry of the finely-divided, co-milled particles and drying the slurried materials to form agglomerated larger particles.

BACKGROUND OF THE INVENTION

Various manufacturing processes for contact solids comprising various metal compounds and mixtures are known in the industry. Solids milling, particle separation, slurrying and drying techniques are well known, and can be performed in batch operations, semi-batch or continuously.

Metal oxide or metal salt raw materials are generally available as a commodity having relatively coarse, non-uniform particles, thus requiring size reduction or comminution prior to making contact solids containing such raw materials. Contact solids products for use as industrial catalysts, sorbents, etc., often require close control of particle size distribution and other physical properties, such as attrition resistance. Mechanical strength is especially important in those industrial process, such as fluidize catalytic cracking (FCC) or other unit operations wherein the contact solids are subject to mechanical handling. Attempts to improve attrition properties have often relied upon binder materials to impart the desired mechanical properties to the chemical agents. US 4,755,499 (Neal et al) relates the importance of attrition resistance in fluid bed solids.

5 US 5,559,067 (Lerner et al) describes in situ processes for making improved zeolitic fluid cracking catalyst by spray drying a mixture of hydrous kaolin, gibbsite and spinel, essentially free from metakaolin, calcining the resulting microspheres to convert the hydrous
10 kaolin to metakaolin. The gibbsite crystals are ground to less than 5 microns prior to slurring.

In US Patent 5,498,731 (Tsurta et al) oxide catalyst is prepared by: reacting a pentavalent vanadium compound and a pentavalent phosphorus compound in an organic solvent
15 in the presence of a reducing agent capable of reducing the pentavalent vanadium to the tetravalent state to produce the crystalline composite oxide particles containing tetravalent vanadium and pentavalent phosphorus; dry-pulverizing the obtained crystalline composite oxide
20 particles in a high-speed gas flow; mixing the pulverized particles with an aqueous solution containing tetravalent vanadium and pentavalent phosphorus to form a slurry, spray-drying the slurry and then calcining.

SUMMARY OF THE INVENTION

25 A novel method for making mixed crystalline solid particles has been found. In the preferred embodiments, an intimate mixture of metal oxides and/or metal salts is formed by dry milling an admixture of coarse solid components to form a finely divided blend of comminuted
30 particles having an average size less than 5 microns (μ), typically less than about 2μ . An aqueous slurry of the admixed solids blend can be spray dried to form larger aggregates having an average size of at least 20μ having superior attrition resistance and uniform particle
35 distribution. The products are useful as contact solids, such as sorbents or catalysts.

5 DETAILED DESCRIPTION OF THE INVENTION

In the following description, units are given as parts by weight and metric units unless otherwise indicated.

Various combinations of metal oxides and salts have been found to be useful for co-milling according to the present invention. For instance, zinc oxide, calcium sulfate (gypsum), silica, basic magnesium silicate (talc), titanium dioxide, USY synthetic faujasite and ZSM-5 zeolites, hydrotalcite, bentonite and various other clays. These metal oxide/salt components may be useful in hydrocarbon conversion catalysis, NO_x/SO_x sorption and other contact processes. For instance US 4,640,825 (Rosenberg) describes ZnO particles in a spray dryer and employed for SO_x abatement.

The contact solids compositions made by this invention may include a combination of inorganic oxides or salts with an inorganic binder. Desirable inorganic oxides include a member selected from the group consisting of oxides or hydroxides of aluminum, calcium, cobalt, copper, iron, magnesium, molybdenum, silicon, titanium, vanadium, zinc, tungsten, strontium, nickel, manganese, zirconium, barium, members of the lanthanide series and mixtures thereof.

The contact solid compositions may be self-bound or may include a binder component to "glue" the inorganic oxides together into the desired shape, such as spheroidal particles. Depending on the application, different binding systems are used, and binders may be added to co-milled metal oxides/salts prior to forming the aqueous slurry.

For example, in more severe high temperature applications such as fluid cracking catalyst (eg- 700-820°C), a hydrothermally stable inorganic binder such as aluminum chlorohydrate or peptized alumina is used.

Effective inorganic binders include sols of aluminum such as aluminum chlorohydrate, peptized aluminas, sols of

5 silica, colloidal silicas, sols of titanium, sols of
zirconium clays such as bentonite, calcined kaolinite,
kaolinite, metakaolin, montmorillonite, chlorite, talc, and
mixtures of these. Desirable inorganic binders include a
sol of aluminum, peptized alumina, a sol of silica,
10 colloidal silica, a sol of titanium, a sol of zirconium, a
clay, and mixtures thereof.

Manufacturing Logistics - The method for making solid
particles according to one aspect of the invention provides
the intimate mixture of solid crystalline metal compounds
15 by the steps of: a) admixing particulate metal compounds to
form a dry solids blend of at least two different
crystalline solids; b) dry milling the blended solids to
produce finely-divided crystalline solids; c) recovering
from the dry milling step a comminuted solids blend having
20 an average particle size of about 1-5 microns; d) storing
the recovered comminuted solids blend in a dry storage
container for subsequent completion of manufacture; e)
transporting a measured portion of the comminuted solids
blend from the storage container to a manufacturing
25 facility; f) forming an aqueous slurry of the transported,
comminuted solids blend; g) drying the aqueous slurry to
form agglomerated particles having an average size range
greater than about 20 microns; and h) recovering dry
agglomerated particles having enhanced attrition resistance
30 and particle size uniformity.

This technique lends itself well to flexible
manufacturing facilities wherein several different
preblended materials comprising the co-milled crystalline
materials are stored under dry conditions until required
35 for entry into the manufacturing stream. Online blending
of multiple pre-blended components by conveyors or the like
can be controlled from a console associated with the

5 slurrying step. Surfactants are added advantageously with the slurried components at this point in the manufacturing process.

For example a mixture of zinc oxide and titanium dioxide in a fixed weight ratio of 1.5:1 ZnO:TiO₂ can be pre-blended and stored for later incorporation into a variety of different contact solids formulations.

Dry Milling Techniques - Existing dry milling and particle separation equipment can be employed in the comminuting step. US 3,531,310 (Goodspeed et al) provides a summary of prior art "micronizer" technology is given in Col. 4 and exemplifies this type of dry milling. A typical micronizer machine is made by Sturdevant and performs dry milling by impelling the solids blend with high pressure dry inert gas against a hard plate surface thereby producing finely-divided crystalline solids and recovering an intimate comminuted solids blend having an average particle size of about 1-5 μ or smaller. Typical micronizer operations produce recovered particles predominantly less than 2 μ size. It is understood by those skilled in the comminuting art that substantially equivalent results can be obtained by alternative dry milling techniques and subsequent particle separation and recovery. Typically, the comminuting step is conducted at ambient temperature or less than 25°C, depending upon the frangibility of the coarse particulates in the feed. Air or inert gas is usually employed as the source of fluid energy for the micronizer milling. Dry gas having a dew point of less than -50°C can assure that no free water is added to the solids during milling.

Slurry Techniques - The finely-divided co-milled solids components are mixed with water, preferably containing

5 about 0.1 to 1 wt% surfactant prior to forming and drying
the contact solid product herein. Surface hydrolysis can
be a significant detriment to many materials, and it is an
advantage of the present invention to provide pre-blended,
dry-milled materials for dispersion in water and spray
10 dried or otherwise manufactured as dry particles in a short
time period, usually less than 1 hour from initial contact
with free water.

Hydrolyzable metal oxides and salts are advantageously
pre-blended and stored in the substantial absence of added
15 water. It is understood that ostensibly dry components,
such as $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ (calcium sulfate monohydrate) contain
bound water; however, such materials do not interfere with
long term storage of pre-blended metal oxide/salt mixtures.

Batchwise or continuous inline feeding of slurry
20 components is well known. Thereafter, the slurry is pumped
or otherwise transported to the spray dryer feed tank.

It is a significant advantage of the present invention
to use limited amounts of water in forming a fluent slurry
for spray drying. By decreasing the amount of water below
25 a weight ratio of 2:1 water:solids (ie - typically 30 wt%
or more solids), energy savings are realized in the drying
step. By maintaining effectively dry solids in admixture
before forming the slurring within, for instance one hour
before drying, surface hydrolysis is avoided or minimized.

30 Surfactants - In the preferred methods, a suitable
alkaline stable or acid stable surfactant is added to the
slurry. Surfactants for improving the physical and
catalytic properties of FCC catalysts are disclosed in US
Patent 5,330,943 (Shi et al). Improved attrition
35 resistance and standard testing (ie- Attrition Index or
'AI') are described by Shi et al, who recommend about 0.25-
4 grams per 5 kg of spray dried product. Preferred acid
stable surfactants are fluorohydrocarbons manufactured

5 under the trade name "DuPont Zonyl TBS" or 3M "FC-95", and
0.01-1 wt % is satisfactory. The use of surfactant is
believed to contribute to attrition resistance by
decreasing the 'blow holes' during spray drying.

10 Spray Drying - Conventional spray drying techniques are
known to the industry, usually withdrawing a slurry
containing sufficient water to form a fluent mixture of
solids and liquid phases, advantageously incorporating a
surfactant to impart homogeneity and mechanical properties
to the resulting dry products. Heat and low pressure
15 permit flashing or rapid evaporation of the liquid phase
from a slurry mist, resulting in agglomeration of smaller
particles to form larger solid, typically having a
spheroidal shape and a particles size distribution in the
20-250 micron (μ) range or larger. In the manufacture of
20 FCC catalyst or additive solids, the particles typically
have an average size of 20-100 μ . In sorbent particles for
fluid bed processes, a larger particle having an average
size of about 150-200 μ may be desired.

To exemplify the invention, the following examples are
25 given. In comparative Examples B1-B4 aspects of the
invention are demonstrate, contact solids consisting
essentially of zinc oxide and calcium sulfate, along with a
minor amount of bentonite clay are compounded, dry milled
and spray dried to obtain SOx-absorbent particles. In one
30 preferred zinc titanate embodiment, the blended metal
oxides contain about 15-65 wt% ZnO, 10-35 wt% TiO₂ and 0-10
wt% bentonite clay or similar binder. In other preferred
embodiments, the blended metal compounds contain about 15-
65 wt% ZnO, 10-35 wt% CaSO₄ and 0-10 wt% bentonite clay.
35 The comminuting step is usually conducted under ambient
conditions at a temperature of about -25 to 25°C. The
aqueous slurry containing about 35 wt% solids is spray

5 dried to form agglomerated particles having an average size of about 120-200 microns. The comminuted solids blend is in contact with free water less than 1 hour before the drying step, thereby minimizing hydration reactions.

10 EXAMPLE A - An attrition-resistant contact solids sulfur oxide sorbent material useful as FCC additive was prepared according to the present invention. A blend of mixed metal oxides, consisting essentially of 21% zinc oxide (ZnO), 14% titanium dioxide (TiO₂), 15% Luzenac 'Cimpact' talc (Mg₃Si₄O₁₀(OH)₂), 10% LaRoche hydrotalcite (HTC), and 40%
15 Thiele 'RC-87' kaolin clay, on an oxide basis, was dry blended. The blend of mixed metal oxide powders were fed, using a vibratory tray feeder, to a Sturdevant micronizer jet mill operated under ambient conditons, at air and feed rates to achieve a ground powder average particle size of
20 less than 3 microns, as measured by laser light scattering, ASTM method D4464.

The ground blend of mixed metal oxides was slurried under high shear to achieve 25-30 percent solids dispersin in a solution containing vanadyl sulfate and cerium oxide
25 to equal 2% vanadium and 12% cerium oxide on the finished catalyst. DuPont 'Zonyl TBS' acid-stable fluorohydrocarbon surfactant is added to the spray drier feed at a rate of about 0.1 part per 100 parts of spray dried powder product. The slurry is then spray dried to yield a 70-80 micron (μ)
30 particle product, having an Attrition Index (AI) of 6.

COMPARATIVE EXAMPLES B1-B4 - A series of comparative samples were prepared using the procedure of Example A, except as noted.

35 EXAMPLE B1 - A blend of mixed metal oxides, consisting of 55 wt% zinc oxide, 9% bentonite, 28% gypsum (CaSO₄), and

5 8% Drierite were dry blended and dry milled in a micronizer to achieve a ground powder average particle size of less than 3 microns. The ground blend of mixed metal oxides was slurried in water to achieve 25-35% solids. Acid-stable surfactant is added, and the slurry is spray dried using a pressure nozzle system to achieve an average spray dried particle of 130 μ .

EXAMPLE B2 - Example B1 is repeated, except the preparation is made without surfactant addition.

15 EXAMPLE B3 - Drierite and calcium sulfate were individually ground to an average particle size of less than 3 microns using the procedure of Example B1. A blend of mixed metal oxides, consisting of 56% unground ZnO, 9% unground Bentonite, 28% ground gypsum, and 7% ground Drierite were dry blended. The blend of powders was slurried in water to 25-35% solids. Acid-stable surfactant is added to the slurry. The slurry is spray dried using a pressure nozzle system to achieve an average spray dried particle of 130 μ .

25 EXAMPLE B4 - Example B3 is repeated, except the preparation is made without the surfactant addition.

TABLE 1

Attrition Data

Materials prepared according to Examples B1-B4 are tested for attrition resistance in a standard milling procedure with weight percent loss by attrition being measured at 5 and 20 hour periods.

Example No.	5 hour loss	20 hour loss
B1	5.7 wt%	10.3 wt %
B2	7.4	19.6
B3	8.9	12.4
B4	9.1	13.5

These data show substantial improvement for the co-milled metal oxide materials, especially with addition of the surfactant in Ex. B1. The invention is further demonstrated by a series of metal oxide formulations employing the procedure of Example A, except as noted.

EXAMPLE C - A zinc oxide/titanium dioxide mixture having a 1.5:1 ZnO:TiO₂ wt.ratio (95 wt%) is blended with 5wt% bentonite and co-milled. The dry milled mixture is slurried with a minor amount of organic binder and surfactant prior to spray drying.

EXAMPLE D - A zinc oxide/titanium dioxide mixture having a 1.5:1 ZnO:TiO₂ wt.ratio (35 wt%) is blended with 10% hydrotalcite powder component (LaRoche HTC) having a particle size range of about 4 to 90 microns (predominantly 15-40 microns), produced by the method of US Patent 5,399,329, with 15% talc and 40% fine kaolin clay.

EXAMPLE E - A dry mixture of 40 wt% ultrastable Y zeolite, 20% silica, 10% Grace WCA alumina, and 30 wt% kaolin clay is co-milled and slurried with binder in water. Surfactant is added to feed slurry during spray drying.

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EXAMPLE F - A dry mixture of 20 wt% ultrastable Y zeolite, 10% clinotilite clay, 20% silica, 10% Grace WCA alumina, and 40 wt% kaolin clay is co-milled and slurried with binder in water. Surfactant is added to feed slurry during spray drying.

EXAMPLE G - A dry mixture of 10 wt% ZSM-5 zeolite (Alsi-Penta 55), 20% silica, 9% monoammonium phosphate, and 61% kaolin clay is co-milled and slurried with Ludox in water. Surfactant is added to feed slurry during spray drying.

TABLE 2**Attrition Data**

Materials prepared according to Examples C-G are tested for attrition resistance in the standard milling procedure with weight percent loss by attrition being measured by standard A.I. test methods.

Example	Part.Size (microns)	Sur. Area m ² /gm.	Attrition Index	D.I./J.I.*
C	96	15	19	22/2.6
D	73	-	4	6/1
E	53	214	24	28/4
F	50	119	11	13/2
G	52	34	1	3/1
B1	120	-	6	7/1

* Davison Index/ Jersey Index

While the invention has been shown by particular examples, there is no intent to limit the inventive concept, except as set forth in the appended claims.

5 Claims:

1. A method for making solid particles containing a mixture of solid crystalline metal oxide and/or salt compounds comprising the steps of:

10 admixing particulate metal compounds to form a dry solids blend of at least two different crystalline solids; comminuting the blended solids by impelling the solids blend with high pressure dry inert gas against a hard plate surface thereby producing finely-divided crystalline solids and recovering a comminuted solids blend having an average
15 particle size of about 1-5 microns;

 forming an aqueous slurry of the comminuted solids blend having a weight ratio of free water to solids less than 2:1;

20 drying the aqueous slurry to form agglomerated particles having an average size range greater than about 20 microns; and

 recovering dry agglomerated particles having enhanced attrition resistance and particle size uniformity.

25 2. The method of Claim 1 wherein the metal compounds comprise about equal parts by weight of calcium sulfate and zinc oxide, and wherein the comminuted solids blend contains at least 50 wt% particles less than 2 microns in size.

30 3. The method of Claim 2 wherein the blended metal compounds contain about 40-60 wt% ZnO, 40-60 wt% CaSO₄ and 0-10 wt% bentonite clay; and wherein the aqueous slurry is spray dried to form agglomerated particles having an average size of about 120-200 microns.

5 4. The method of Claim 1 wherein the comminuted solids blend is in contact with free water less than 1 hour before the drying step, thereby minimizing hydration reactions.

5. The method of Claim 1 wherein the comminuting step is conducted at a temperature of not greater than 25°C.

10 6. The method of Claim 1 wherein the dry gas has a dew point of less than -50°C.

7. The method of Claim 1 wherein the aqueous slurry contains surfactant comprising acid stable fluorohydrocarbon.

15 8. A method for making solid particles containing a mixture of solid crystalline calcium sulfate and zinc oxide compounds comprising the steps of:

 admixing particulate calcium sulfate and zinc oxide to form a dry solids blend of crystalline solids;

20 dry milling the blended solids to produce finely-divided crystalline solids;

 recovering from the dry milling step a comminuted solids blend having an average particle size of about 1-5 microns;

25 forming an aqueous slurry containing a surfactant and the comminuted solids blend having a weight ratio of free water to solids less than 2:1;

 spray drying the aqueous slurry immediately after adding free water, thereby forming agglomerated particles having an average size range greater than about 20 microns; and

30

 recovering dry agglomerated particles having enhanced attrition resistance and particle size uniformity.

5 9. The method of Claim 8 wherein the crystalline solids
comprise about equal parts by weight of calcium sulfate and
zinc oxide, and wherein the comminuted solids blend
contains at least 50 wt% particles less than 2 microns in
size.

10 10. The method of Claim 9 wherein the blended metal
compounds contain about 40-60 wt% ZnO, 40-60 wt% anhydrous
and/or hydrated CaSO₄, and 0-10 wt% bentonite clay; and
wherein the aqueous slurry is spray dried to form
agglomerated particles having an average size of about 20-
15 200 microns.

11. The method of Claim 8 wherein the comminuted solids
blend is in contact with free water less than 1 hour before
the drying step, thereby minimizing hydration reactions.

12. The method of Claim 8 wherein the aqueous slurry
20 contains 0.01-1 wt% surfactant comprising acid stable
fluorohydrocarbon.

13. A method for making fluidizable solid catalyst
particles containing a mixture of catalytically-active
solid crystalline metal oxide material and at least one
25 other crystalline material comprising a metal compound
comprising the steps of:

admixing coarse particulate metal materials to form a
dry solids blend of at least two different particulate
crystalline solids;

30 comminuting the blended solids by impelling the solids
blend with high pressure dry inert gas against a hard plate
surface thereby producing finely-divided crystalline solids

5 and recovering a comminuted solids blend having an average particle size less than 2 microns;

 forming an aqueous slurry of the comminuted solids blend containing an acid stable fluorohydrocarbon surfactant;

10 drying the aqueous slurry to form agglomerated particles having an average size range greater than about 20 microns; and

 recovering dry agglomerated catalytic particles having enhanced attrition resistance and particle size uniformity.

15 14. The method of Claim 13 wherein the metal oxide material comprises a cracking catalyst additive.

15. The method of Claim 13 wherein the metal oxide material comprises zeolite cracking catalyst.

5 16. A method for making solid particles containing a mixture of solid crystalline metal oxide and/or salt compounds comprising the steps of:

 admixing particulate metal compounds to form a dry solids blend of at least two different crystalline solids;

10 dry milling the blended solids to produce finely-divided crystalline solids;

 recovering from the dry milling step a comminuted solids blend having an average particle size of about 1-5 microns;

15 storing the recovered comminuted solids blend in a dry storage container for subsequent completion of manufacture;

 transporting a measured portion of the comminuted solids blend from the storage container to a manufacturing facility;

20 forming an aqueous slurry of the transported, comminuted solids blend;

 drying the aqueous slurry to form agglomerated particles having an average size range greater than about 20 microns; and

25 recovering dry agglomerated particles having enhanced attrition resistance and particle size uniformity.

17. The method of Claim 16 wherein the dry milling step is conducted in a micronizer comminuting mill.

30 18. The method of Claim 16 wherein a plurality of different comminuted solids blends are transported from storage containers and admixed in the aqueous slurry.

19. The method of Claim 16 wherein the comminuted solids blend is in contact with free water less than 1 hour before the drying step, thereby minimizing hydration reactions.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/18169

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C01B 7/00; B01J 8/00

US CL : 423/244.01, 244.06, 244.08; 502/64, 68, 80, 514

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/244.01, 244.06, 244.08; 502/64, 68, 80, 514

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,498,731 A (TSURITA et al.) 12 March 1996 (12-03-96), column 4, line 43 - column 7, line 67.	1 & 4-6
Y	US 5,559,067 A (LERNER et al.) 24 September 1996 (24-09-96), column 5, line 40 - column 9, line 41.	1, 4-7, 13-19
Y	US 5,330,943 A (SHI et al.) 19 July 1994 (16-07-94), see the entire document.	1-19
Y	US 5,512,097 A (EMMER) 30 April 1996 (30-04-96), column. 4-6.	1-12
Y	US 4,931,264 A (ROCHELLE et al.) 05 June 1990 (05-06-90), column. 14, lines 5-50.	1-12
Y	US 4,640,825 A (ROSENBERG) 03 February 1987 (03-02-87), column. 5-7.	1-12

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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